Adsorption processes for gas separation

Marina Micari

Lecture 8

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Intended learning outcome

- Understand how separation via adsorption works

- Describe mass transfer mechanisms inside the adsorption column

- Learn how to simulate adsorption processes

Agenda

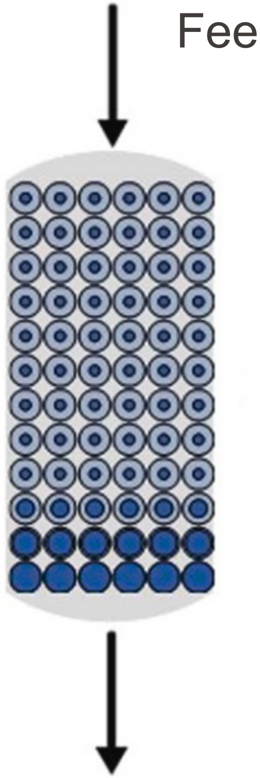
THEORY

- What is an adsorption column?
- What are the involved mass transfer mechanisms?
- How to model the adsorption column?
- How to design the adsorption-desorption cycle?

EXERCISE

✓Calculate working capacity based on the adsorption isotherms

Adsorption process

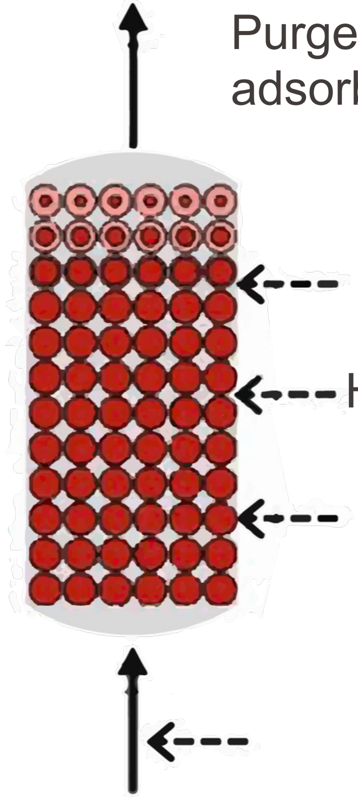


Feed

Loaded sorbent

Fresh sorbent

Outlet stream - lean in the adsorbed component



Purge enriched in the
adsorbed component

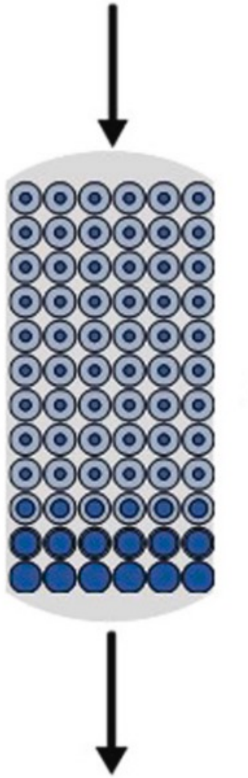
Hot loaded sorbent

Heat

Hot fresh sorbent

Purge

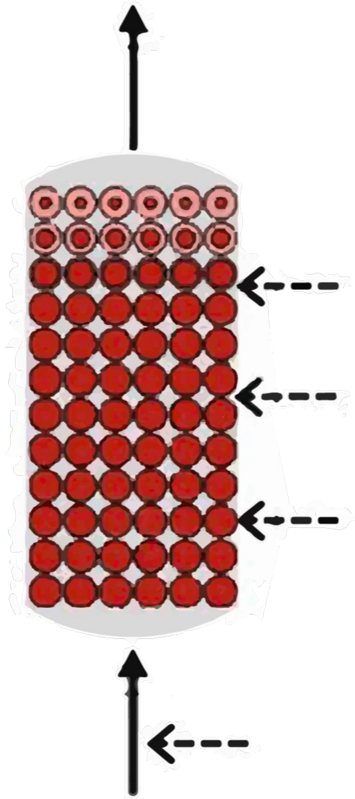
Adsorption process



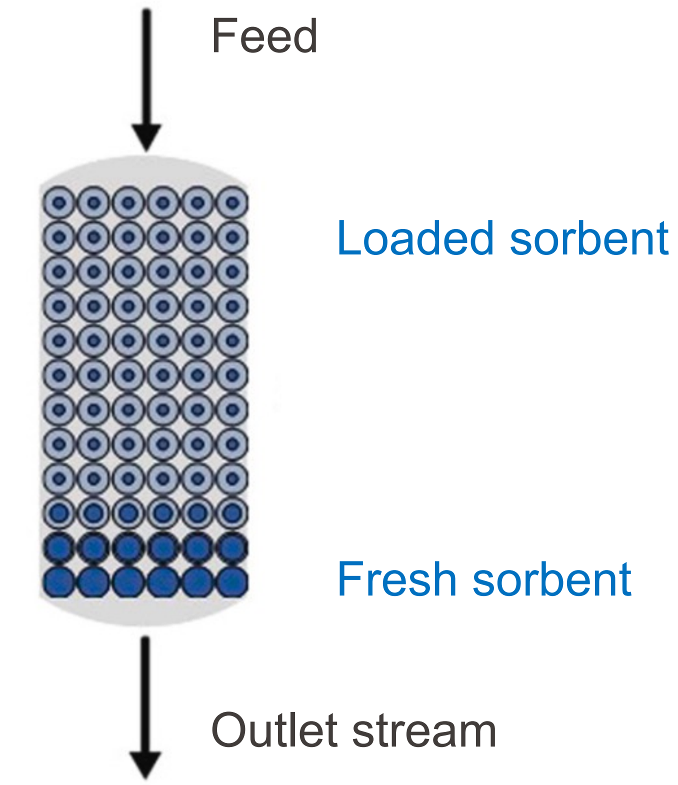
Mass-separating agent: solid sorbent

Separating mechanism: partitioning between fluid and solid phases

Reversing agent: pressure or temperature change

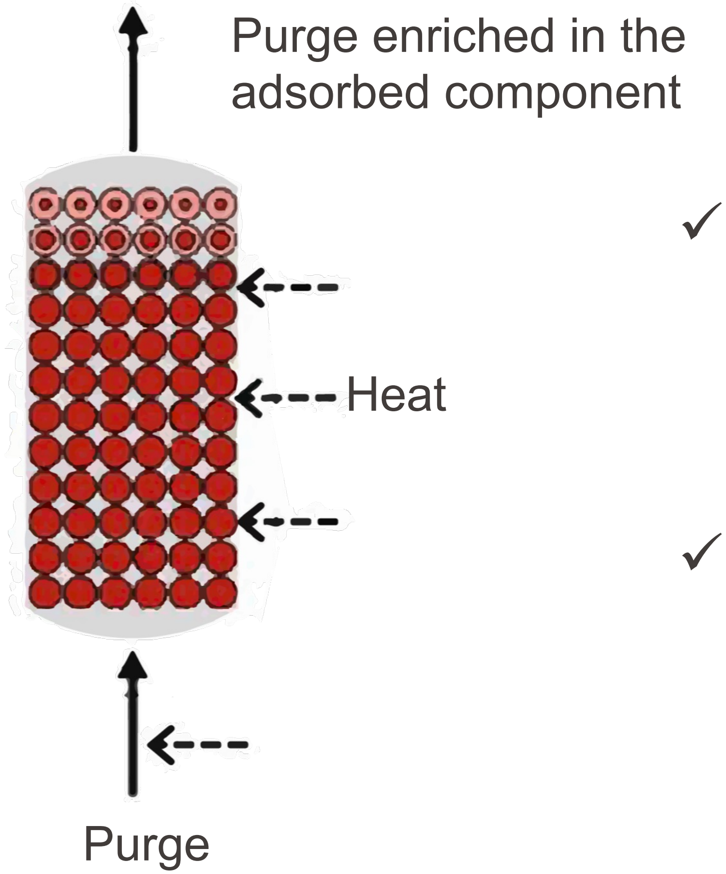


Adsorption – sorbent properties



- ✓**Surface area [m^2/g]:** influences the adsorption capacity of the material
- ✓**Porosity [-]:** fraction of the particle volume that is empty. The higher the porosity, the lower the particle density
- ✓**Tortuosity [-]:** ratio between the length of the tortuous flow path and the length of the straight line.
- ✓**Bulk density [kg/m^3]:** mass of sorbent per volume of the column. It depends on the porosity of the particles and on the packing inside the column

Adsorption process – definitions



- ✓**working capacity [mol/kg]:** total amount of the desired component obtained (desorbed) per kg of sorbent material
- ✓**product purity [-]:** fraction of the desired component in the outlet desorption stream

Adsorption process - definitions

✓ **heat of adsorption [kJ/mol]:** indicates the strength of the adsorption between the sorbent and the component

physisorption	**chemisorption**
weak interactions	chemical bond
$\Delta H < 50$ kJ/mol	$\Delta H \sim 70\text{-}240$ kJ/mol

The higher the heat of adsorption, the higher the heat consumption of the process

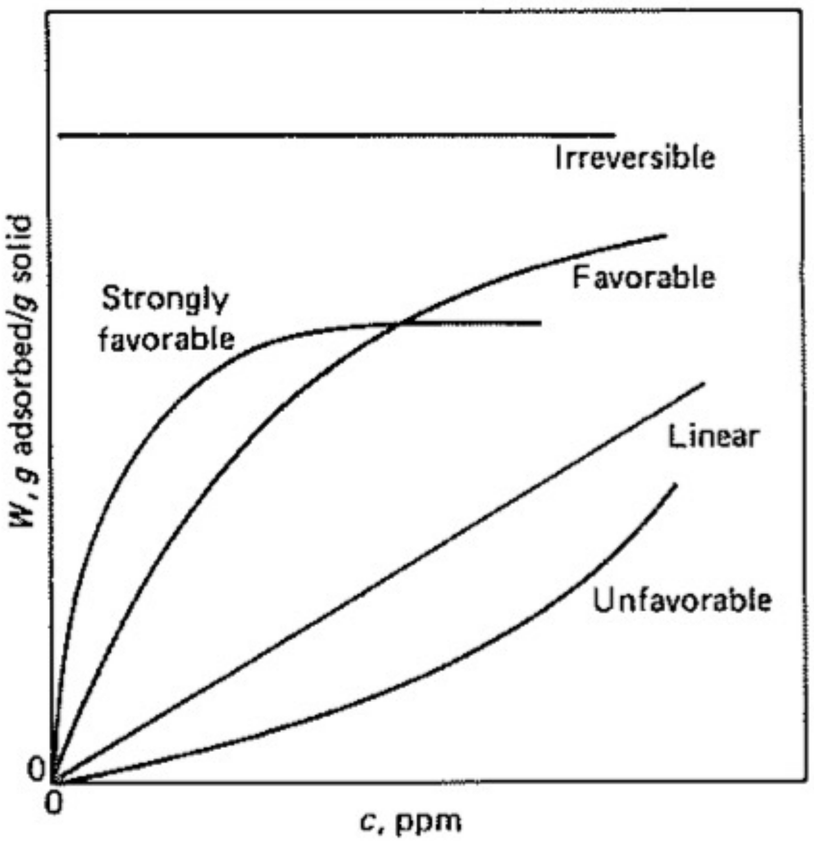
How to model adsorption?

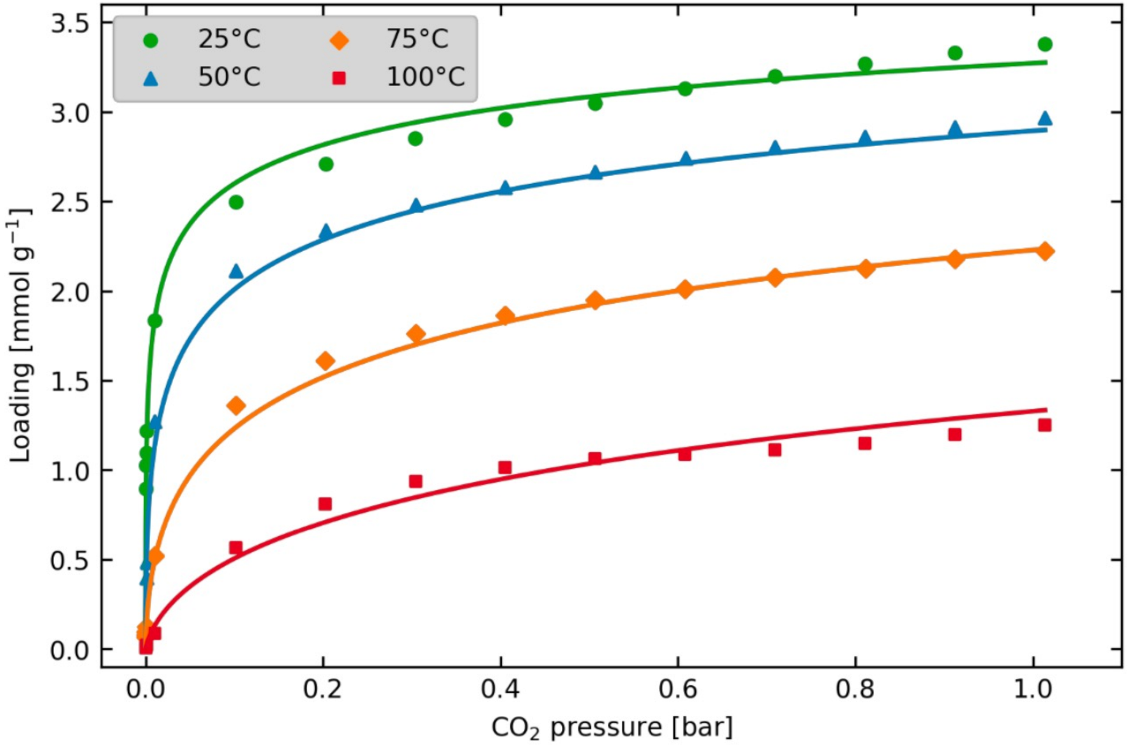
2 key facets:

- Adsorption equilibrium → adsorption isotherms
- Dinamic behaviour → kinetic models for mass transfer

Adsorption equilibrium

- **Adsorption isotherms**: equilibrium uptake of a component into the sorbent at a given temperature as a function of the partial pressure





From Young et al., Energy and Environmental Science 2021

Models for adsorption isotherms (single component)

- Langmuir and Sips isotherms

saturation capacity

equilibrium constant for adsorption

$$q_i^* = \frac{q_{si}(K_i P_i)^{s_i}}{1 + (K_i P_i)^{s_i}}$$

accounts for the inhomegeneity of the adsorption surface.
If the surface is assumed to be homogeneous, s_i is equal to 1 (**Langmuir isotherm**)

adsorbed phase concentration in equilibrium with the gas phase

Models for adsorption isotherms (single component)

- Toth isotherm: extension of the Langmuir to improve the fit at high and low pressure ranges

saturation capacity

adsorption affinity
(function of the heat of adsorption)

$$q_i^* = \frac{q_{si} b(T) P_i}{\left(1 + \left(b(T)P_i\right)^{\tau(T)}\right)^{\frac{1}{\tau(T)}}}$$

adsorbed phase concentration in equilibrium with the gas phase

accounts for surface heterogeneity

Models for adsorption isotherms (single component)

- Freundlich isotherm: takes into account the interactions between adsorbed molecules (often used in the low temperature regime)

$$q_i^* = b\, {P_i}^m$$

b, m are constant derived empirically

Model for adsorption isotherms (multi-component)

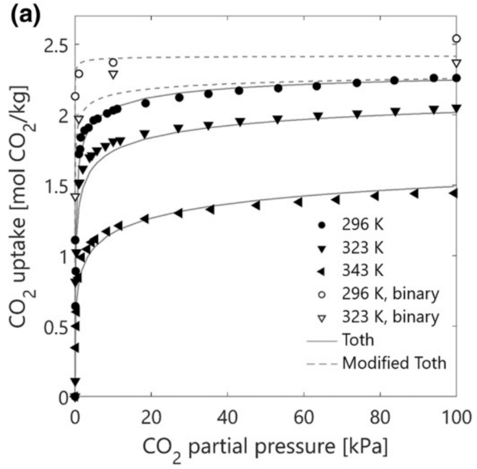
- Multicomponent Sips isotherm: extension of the pure component isotherm where the same coefficients of the pure isotherms can be used

$$q_i^* = \frac{q_{si}(K_i P_i)^{s_i}}{1 + \sum_i (K_i P_i)^{s_i}}$$

- Empirical models based on Toth isotherm to describe co-adsorption

$$q_\infty(T, q_{\mathrm{H_2O}}) = q_\infty(T)\left(\frac{1}{1 - \gamma q_{\mathrm{H_2O}}}\right)$$

$$b(T, q_{\mathrm{H_2O}}) = b(T)(1 + \beta q_{\mathrm{H_2O}})$$

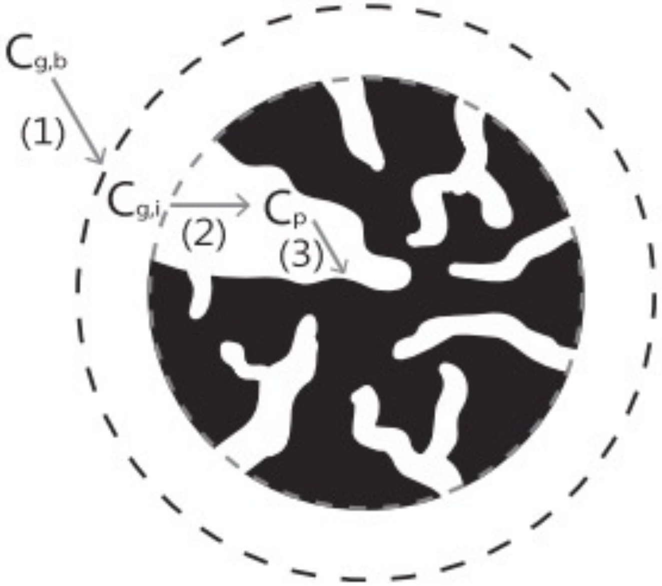


Dynamic - mass transfer mechanisms

- Convection from the bulk to the surface film of the particle
- Diffusion through the fluid film around the particle
- Diffusion through the pores to internal adsorption sites

Typically the rate-determining step

- Physical adsorption (practically instantaneous → fluid and surface at equilibrium)
- Chemical reaction with the functional groups (chemisorption)



From Bos et al., Chemical Engineering Journal 2018

Mass transfer equation

Linear Driving Force model: simplified approach to lump the kinetic resistances

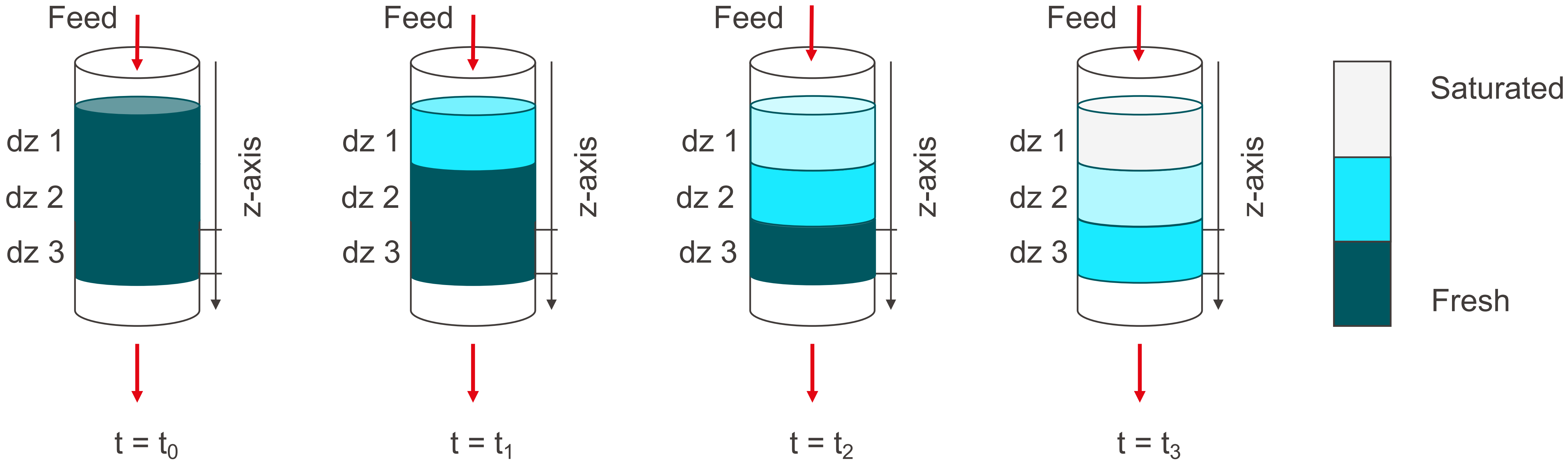
$$\frac{\partial q_i}{\partial t} = k_{LDF,i}(q_i^* - q_i)$$

current uptake

rate constant [s^{-1}]

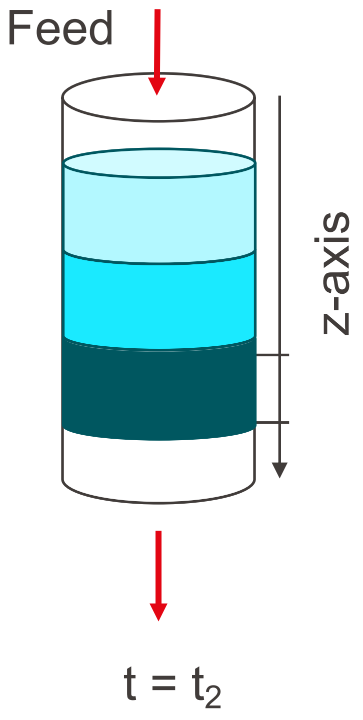
maximum uptake (from the isotherm)

Modelling of an adsorption column



Variation in time and space

Modelling of an adsorption column



Assumptions

- the fluid is an ideal gas,
- the flow is described by an axially dispersed plug flow model,
- negligible temperature and concentration gradient along the radius,
- thermal equilibrium between the fluid and the sorbent,
- heat of adsorption, heat capacities and mass transfer coefficient are temperature independent,
- mass transfer resistance described using a linear driving force model (LDF).

Mass balances

- Total mass balance: $\frac{dc}{dt} = convective\ term\ (u, c)\ - adsorption\ term \left(\frac{dq_{tot}}{dt}\right)$

  c in mol/m^3

$$\overbrace{\frac{\partial}{\partial z}(u\ c)}^{\textbf{convective term}} + \overbrace{\varepsilon_t \frac{\partial c}{\partial t}}^{\textbf{accumulation}} + \overbrace{(1-\varepsilon_b)\rho_p \sum_i \frac{\partial q}{\partial t}}^{\textbf{adsorption term}} = 0$$

if *u* is constant
this is discretized as:

$$\frac{u_o c\ -\ u_o(c+dc)}{\Delta L}$$

total void fraction
in the column

void fraction
in the bed

density of the particle
[$kg_{sorbent}/m^3_{sorbent}$]

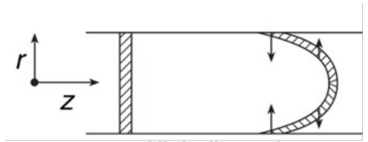
$$\varepsilon_t = \varepsilon_b + \varepsilon_p(1-\varepsilon_b)$$

void fraction in the particle

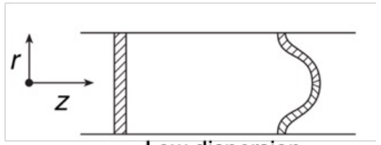
Mass balances

- Mass balance on the component

$$\overbrace{-D_L \varepsilon_B \frac{\partial^2 c_i}{\partial z^2}}^{\textbf{dispersion term}} + \overbrace{\frac{\partial}{\partial z}(u\, c_i)}^{\textbf{convective term}} + \overbrace{\varepsilon_t \frac{\partial c_i}{\partial t}}^{\textbf{accumulation}} + \overbrace{(1-\varepsilon_b)\rho_p \frac{\partial q_i}{\partial t}}^{\textbf{adsorption term}} = 0$$



High dispersion



Low dispersion

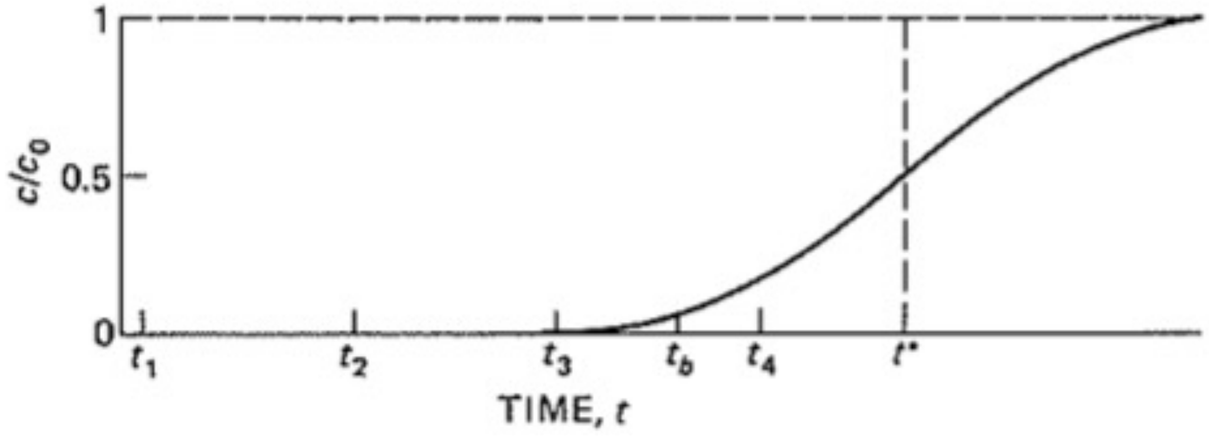
axial dispersion (backmixing) coefficient [m²/s]: measure of the deviation from the ideal plug flow (spread of the concentration profile along the axial direction)

$$D_L = \gamma_1 D_m + \gamma_2 d_p \, {}^{u}/_{\varepsilon_b}$$

D_m molecular diffusion [m²/s]

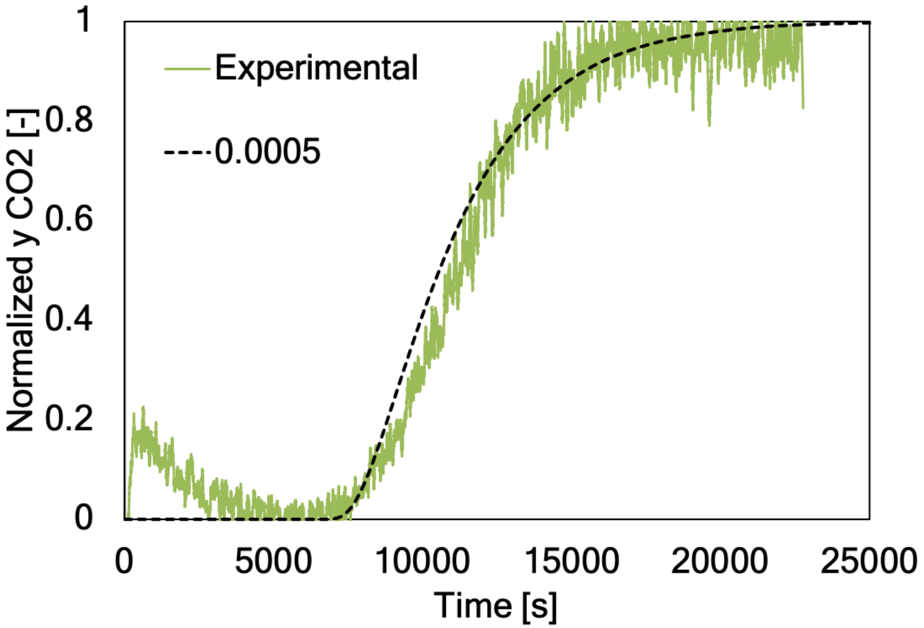
γ_1, γ_2 account for the tortuosity and the turbulent mixing (0.7 and 0.5)

Breakthrough curve
Derivation of the mass transfer coefficient



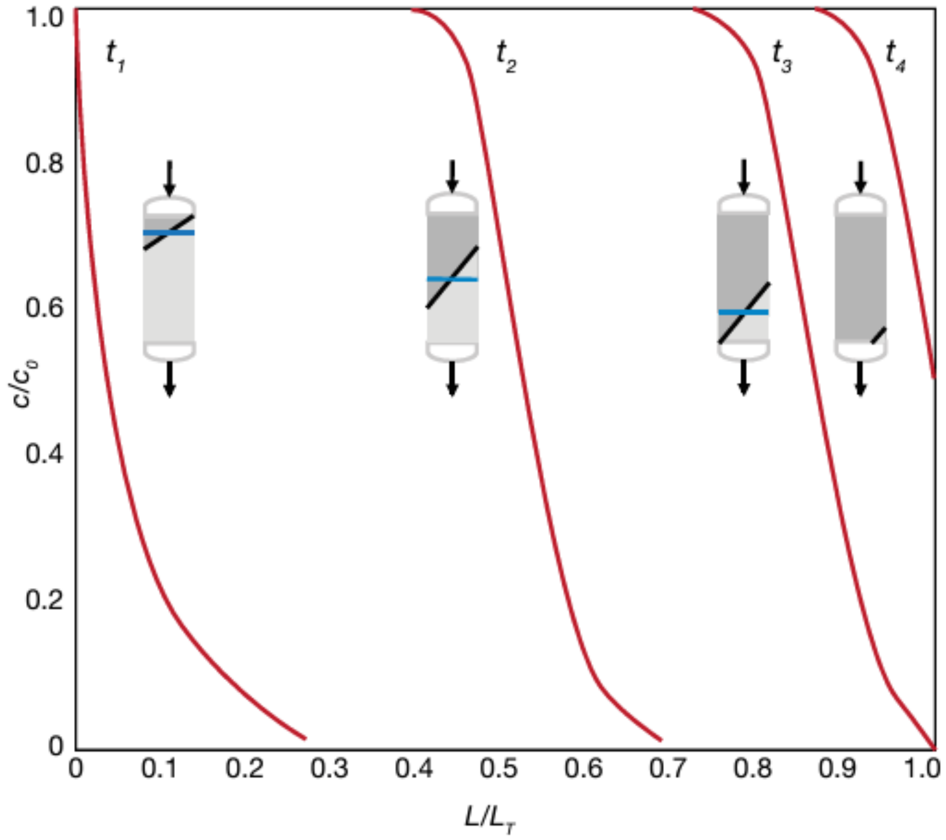
Breakthrough curve:
outlet concentration vs. time

k_{LDF} is derived from fitting the simulated breakthrough to the experimental one

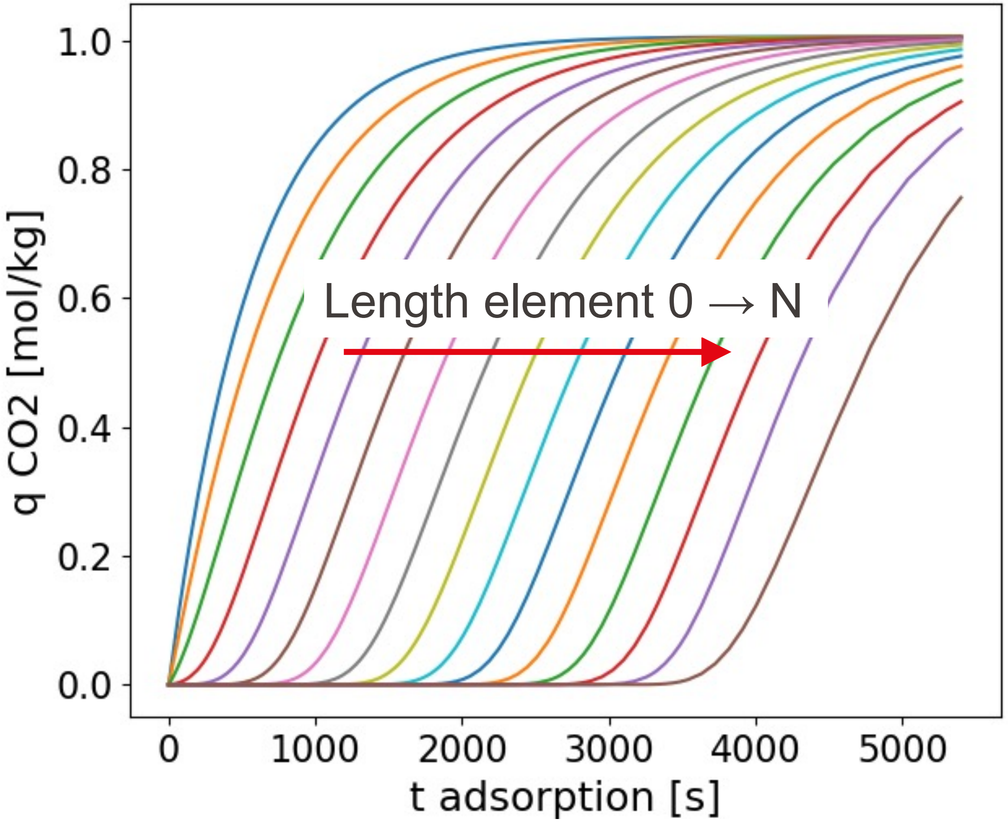


Concentration and uptake patterns

Concentration in the fluid phase as function of **bed length** at different times



Uptake in the solid phase as function of **time** at different lengths



Mass transfer zone moves along the length of the column with time

Energy balance

$$\overbrace{(\varepsilon_t C_G + \rho_b C_s + \rho_b C_{ads})\frac{\partial T}{\partial t}}^{\substack{\textbf{accumulation term}\\ \text{(phases in equilibrium)}}} \overbrace{- \varepsilon_t \frac{\partial p}{\partial t}}^{\substack{\textbf{T variation}\\ \textbf{with P}}} \overbrace{+ u C_G \frac{\partial T}{\partial z}}^{\substack{\textbf{convection}\\ \textbf{term}}} \overbrace{- \rho_b \sum_i (-\Delta H_i)\frac{\partial q_i}{\partial t}}^{\substack{\textbf{adsorption}\\ \textbf{term}}} \overbrace{+ 2\frac{h_L}{R_i}(T - T_w)}^{\substack{\textbf{heat transfer}\\ \textbf{with the wall}}} \overbrace{- \varepsilon_b \frac{\partial}{\partial z}\left(K_L \frac{\partial T}{\partial z}\right)}^{\substack{\textbf{dispersion}\\ \textbf{term}}} = 0$$

heat capacity of the fluid

heat capacity of the solid

heat capacity of the adsorbed species

heat of adsorption (exotermic reaction)

h_L: heat transfer coefficient from inside the column to the wall
R_i: internal radius

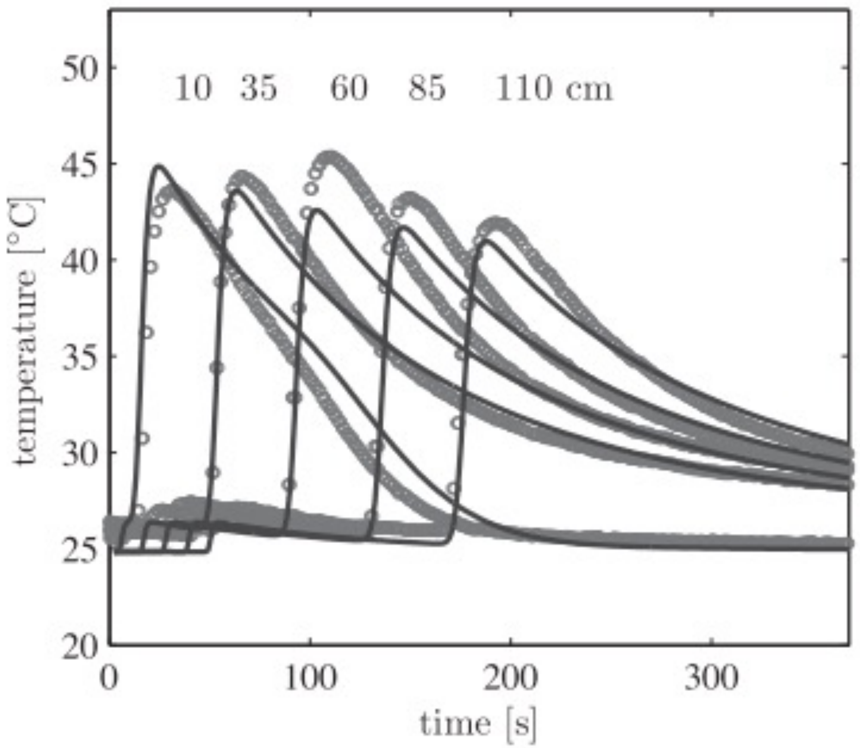
K_L: axial thermal conductivity [W/(m K)]

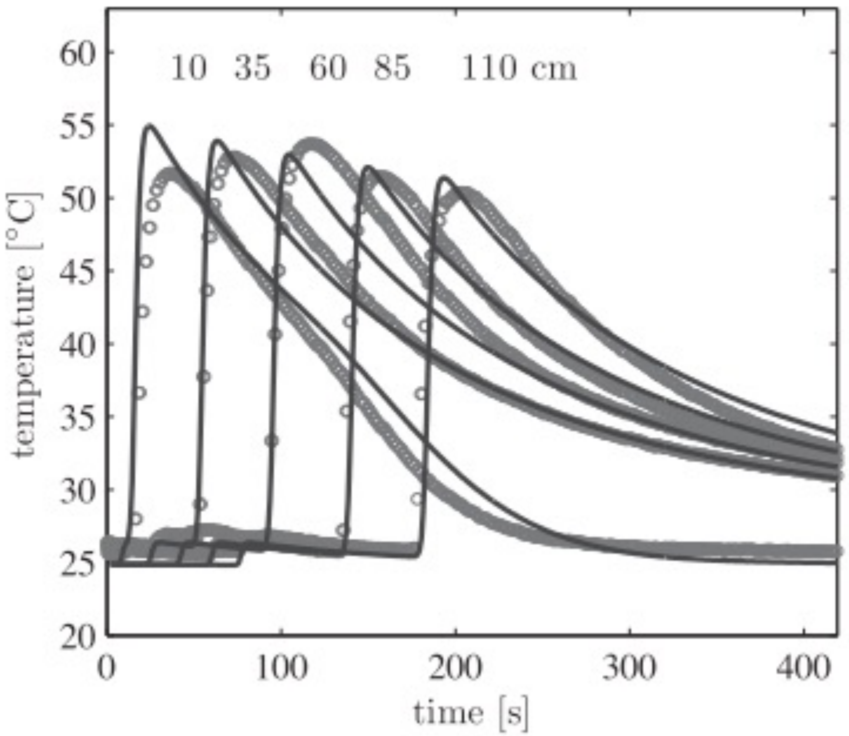
$$K_L = D_L\, C_G$$

Speaker

Temperature patterns

What could be the reason of the difference between the two charts?





From Casas et al., Separation and Purification Technology 2013

Pressure drops

- Ergun equation → to derive gas velocity in the column for a given pressure gradient

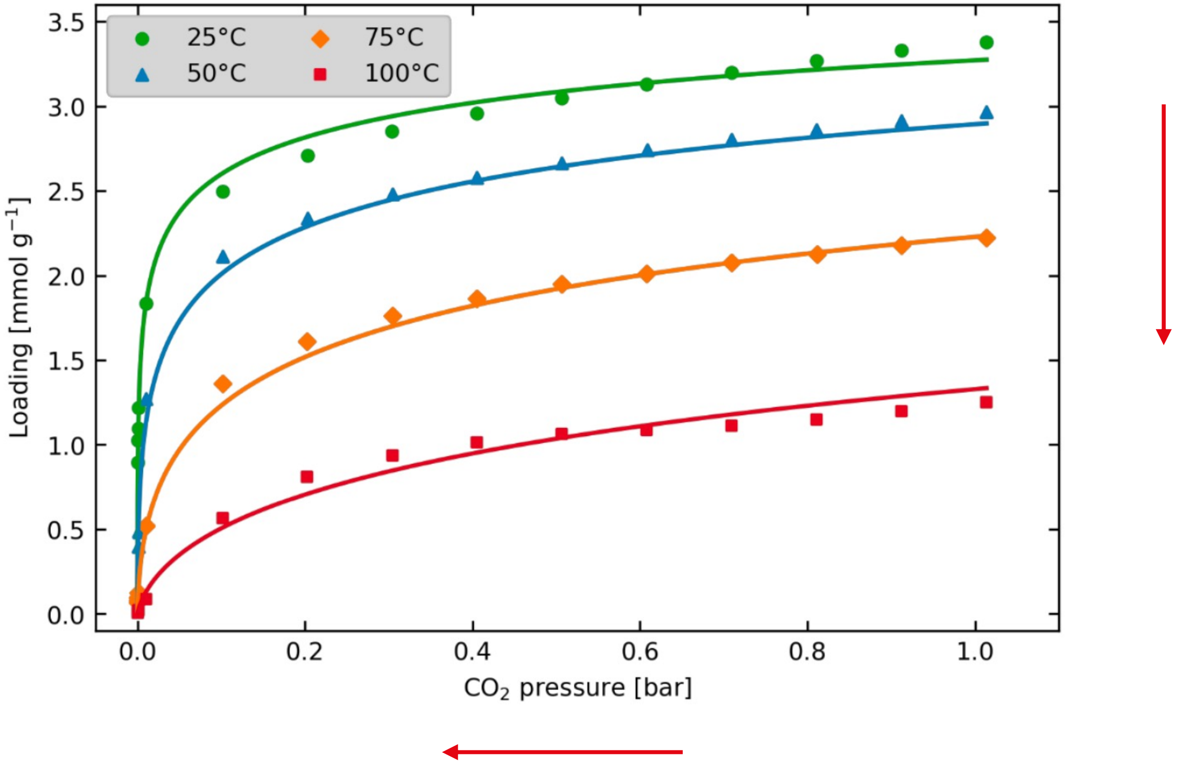
$$\frac{\partial p}{\partial z} = -\frac{150\,\mu(1-\varepsilon_b)^2}{{\varepsilon_b}^3{d_p}^2}u - \frac{1.75(1-\varepsilon_b)\rho}{{\varepsilon_b}^3 d_p}|u|u$$

μ: dynamic viscosity of the fluid [Pa s]

ρ: fluid density [kg/m^3]

How to perform desorption

We need operating conditions that do not favour adsorption:
the **equilibrium uptake decreases** and the adsorbed components tend to desorb

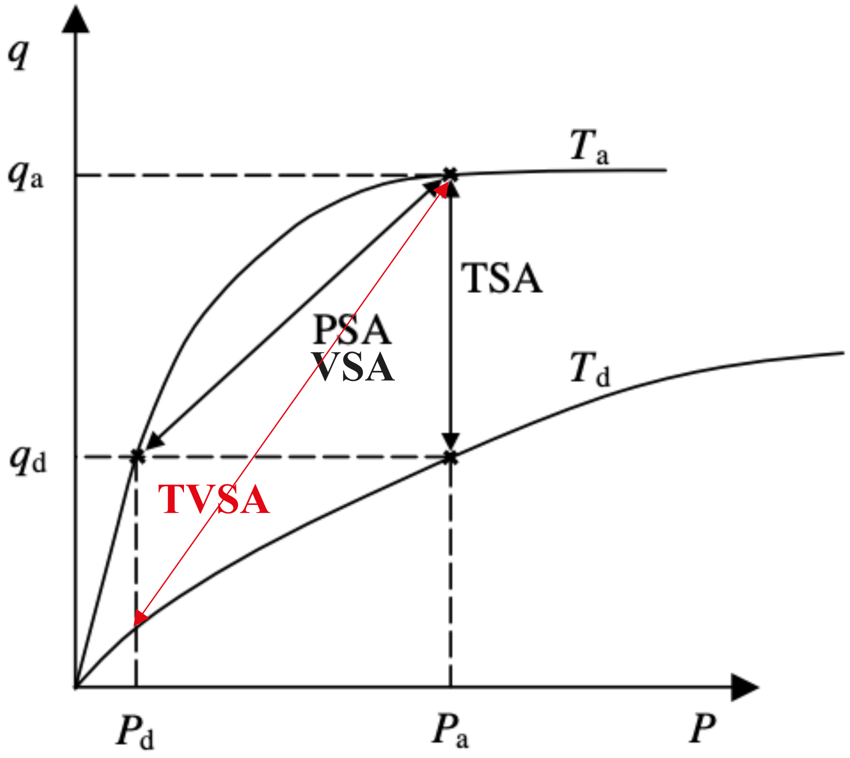


increasing the temperature

decreasing the pressure

Adsorption-desorption cycle

- PSA: pressure swing adsorption
- VSA: vacuum swing adsorption
- TSA: temperature swing adsorption
- TVSA: temperature vacuum swing adsorption

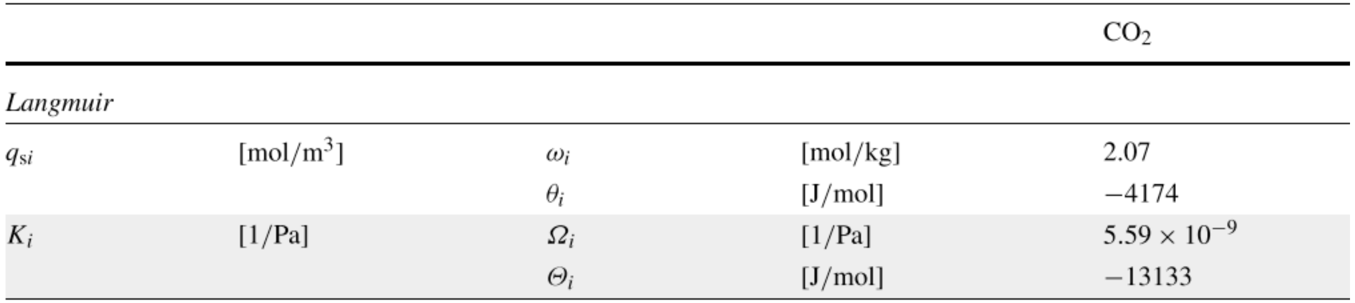


Impact of the properties on the process

▪ Adsorption isotherms	➢ Working capacity
▪ Mass transfer coefficient	➢ Rate of mass transfer
▪ Density (bulk and particle)	➢ Mass of sorbent per column
▪ Heat capacity	➢ Heat required to increase T
▪ Heat of adsorption	➢ Heat required to perform desorption
▪ Heat transfer coefficient	➢ Rate of heat transfer

Exercise 1 – working capacity

We use adsorption to capture CO_2 from a CO_2-H_2 mixture containing 25% CO_2 and 75% H_2 (adsorption of H_2 is negligible).
For a given sorbent (activated carbons), calculate the equilibrium working capacity when adsorption occurs at ambient temperature (25ºC) and 15 bar, and desorption occurs at 100ºC and ambient pressure.



				CO_2
Langmuir				
q_{si}	$[\mathrm{mol/m^3}]$	ω_i	$[\mathrm{mol/kg}]$	2.07
		θ_i	$[\mathrm{J/mol}]$	-4174
K_i	$[1/\mathrm{Pa}]$	Ω_i	$[1/\mathrm{Pa}]$	5.59×10^{-9}
		Θ_i	$[\mathrm{J/mol}]$	-13133

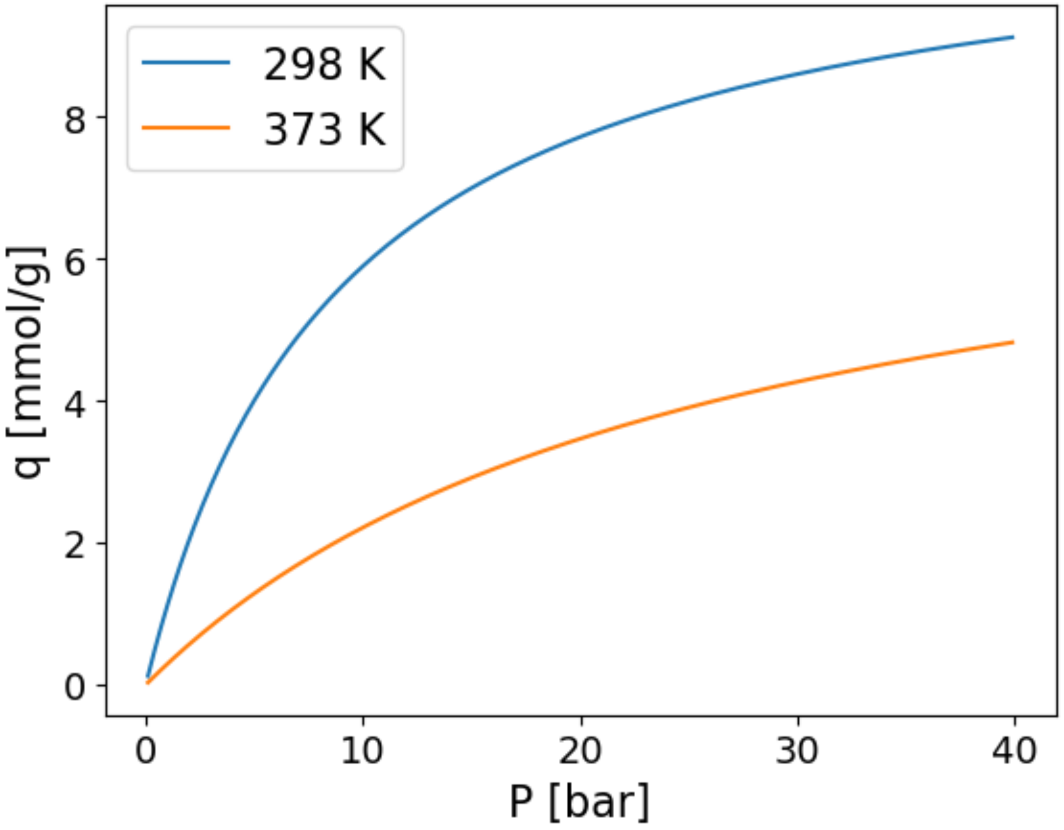
$$q_i^* = \frac{q_{si}(K_i P_i)^{s_i}}{1 + (K_i P_i)^{s_i}}$$

$$q_{si} = \omega_i \exp\left(\frac{-\theta_i}{RT}\right)$$

$$K_i = \Omega_i \exp\left(\frac{-\Theta_i}{RT}\right)$$

From Casas et al., Separation and Purification Technology 2013

Exercise 1 - solution



$$q_{ads} = Langmuir(\omega, \theta, \Omega, \Theta, R, T_{ads}, P_{tot,ads} \times X_f)$$

$$q_{des} = Langmuir(\omega, \theta, \Omega, \Theta, R, T_{des}, P_{tot,des})$$

$$working\ capacity = q_{ads} - q_{des} = 3\ {}^{mmol}/_{g}$$

Exercise 2

We use adsorption to capture CO_2 from a flue gas containing 10% CO_2 and 90% N_2.

For a given sorbent (zeolite 13X), calculate the equilibrium working capacity when:

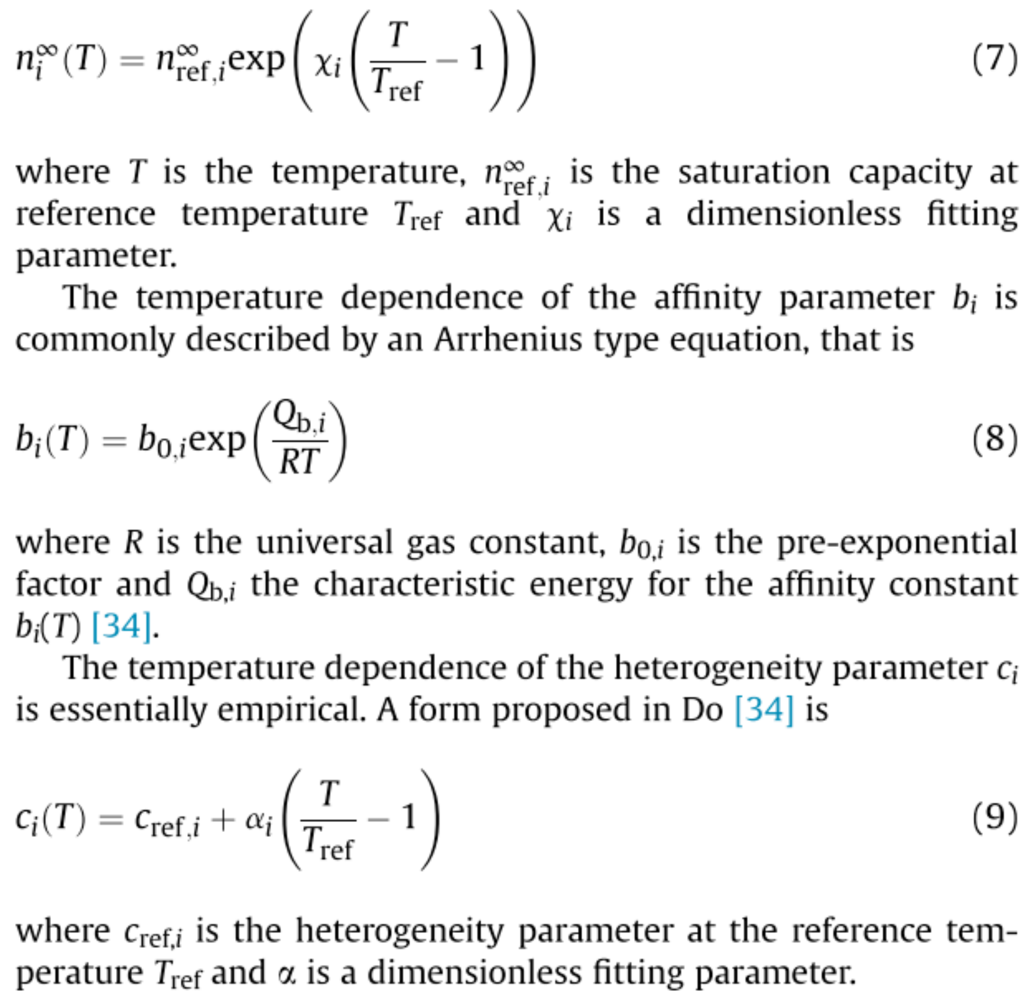
- adsorption occurs at ambient temperature (25ºC) and ambient pressure, and desorption occurs at 100ºC and ambient pressure;
- adsorption occurs at ambient temperature (25ºC) and pressure of 20 bar, and desorption occurs at ambient temperature and ambient pressure;
- adsorption occurs at ambient temperature (25ºC) and ambient pressure, and desorption occurs at ambient temperature and vacuum pressure of 0.05 bar;
- adsorption occurs at ambient temperature (25ºC) and ambient pressure, and desorption occurs at 100ºC and vacuum pressure of 0.1 bar.

To which processes, do these different operating conditions correspond?

What happens if T of adsorption and T of desorption change?

- What happens when CO2 concentration decreases to 4% and to 0.04% (DAC)?

Exercise 2 – isotherm for Zeolite 13X



$$n_i^\infty(T) = n_{\text{ref},i}^\infty \exp\left(\chi_i\left(\frac{T}{T_{\text{ref}}} - 1\right)\right) \qquad (7)$$

where T is the temperature, $n_{\text{ref},i}^\infty$ is the saturation capacity at reference temperature T_{ref} and χ_i is a dimensionless fitting parameter.

The temperature dependence of the affinity parameter b_i is commonly described by an Arrhenius type equation, that is

$$b_i(T) = b_{0,i}\exp\left(\frac{Q_{b,i}}{RT}\right) \qquad (8)$$

where R is the universal gas constant, $b_{0,i}$ is the pre-exponential factor and $Q_{b,i}$ the characteristic energy for the affinity constant $b_i(T)$ [34].

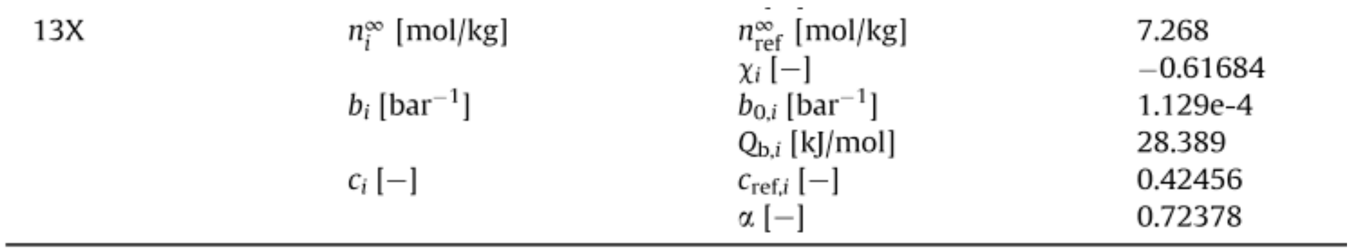
The temperature dependence of the heterogeneity parameter c_i is essentially empirical. A form proposed in Do [34] is

$$c_i(T) = c_{\text{ref},i} + \alpha_i\left(\frac{T}{T_{\text{ref}}} - 1\right) \qquad (9)$$

where $c_{\text{ref},i}$ is the heterogeneity parameter at the reference temperature T_{ref} and α is a dimensionless fitting parameter.

$$n_i = \frac{n_i^\infty (b_i P)^{c_i}}{1 + (b_i P)^{c_i}}$$

Parameters for the pure component Sips isotherm for CO_2



13X	n_i^∞ [mol/kg]	n_{ref}^∞ [mol/kg]	7.268
		χ_i [−]	−0.61684
	b_i [bar^{-1}]	$b_{0,i}$ [bar^{-1}]	1.129e-4
		$Q_{b,i}$ [kJ/mol]	28.389
	c_i [−]	$c_{\text{ref},i}$ [−]	0.42456
		α [−]	0.72378

T_{ref} = 25ºC

n_i in the formula correspond to q_i^* (equilibrium uptake)

From Hefti et al., Microporous and Mesoporous Materials 2015